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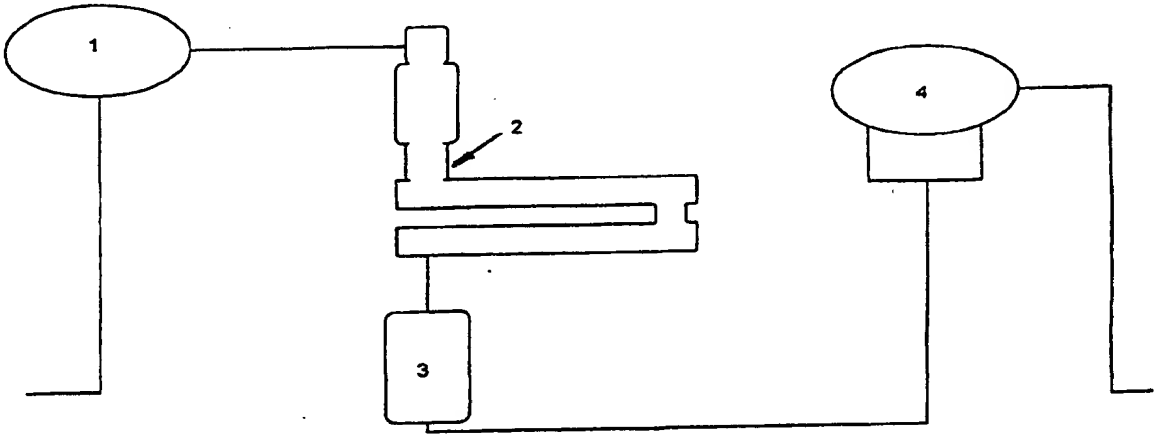
With amended claims.

(54) Title: BLEACHING OF LIGNOCELLULOSIC PULP WITH OZONE AND PERACID



(57) Abstract

The present invention relates to a method of bleaching lignocellulosic fiber material in a combination step with ozone and peracid, such as peracetic acid, $Z_{HC}Paa_{MC}$. The invention preferably relates to the bleaching of sulphate pulp. The pulp is ozone treated in a HC step in an ozone reactor, whereafter the pulp is diluted with water or white water, and peracid is added prior to an MC bleaching tower with subsequent washing.

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Bleaching of lignocellulosic pulp with ozone and peracid.

The present invention relates to a method of bleaching lignocellulosic fiber material in a combination step with ozone and peracid, such as peracetic acid, $Z_{HC}Paa_{MC}$. The invention preferably is directed to the bleaching of sulphate pulp. The pulp is treated with ozone in an HC step in an ozone reactor, where after the pulp is diluted with water or white water, and peracid is added prior to a MC bleaching tower, with subsequent washing.

At commercial operation, ozone has recently been introduced as a bleaching chemical at the bleaching of pulp, in order to minimize the use of bleaching chemicals, and, respectively, to increase the bleaching without using chlorine chemicals by using a strong delignification chemical. Owing to its good delignification capability and relatively low price, in relation to its high specific oxidation potential, ozone is a costeffective complement to other chemicals in bleaching sequences, in which no chlorine chemicals are used. It is difficult by these sequences to achieve long range bleaching without serious carbohydrate degradation, which deteriorates the strength of the fiber material.

Ozone, on the whole, causes considerable degradation, which distributes itself between moderate direct carbohydrate degradation and alkali sensitivity, due to the introduction of carbonyl groups into the cellulosa, which causes rapid degradation in a subsequent alkaline step. Due to the alkali sensitivity, the value obtained at the viscosity analysis is lower than what corresponds to real polymerisation degree of the carbohydrate material. The higher real polymerisation degree is determined simply by a boron hydride reduktion of the pulp before the viscosity analysis. The total degradation in the ozone step would be reduced substantially, if boronhydride steps are introduced into the bleaching sequence

after the ozone step. For several reasons, this is practically not possible. Until now no applicable solution has been proposed, by which this alkali instability could be avoided.

Alternatives to ozone are peracids, such as performic acid, peracetic acid and persulphate (Caros acid), which at suitable conditions yield low carbohydride degradation. Bleaching with these can be carried out in existing equipment found in traditional bleach plants, contrary to ozone. A serious disadvantage, however, is that they are considerably more expensive than ozone, in relation to their oxidation capability.

At the present intention the costeffective delignification of ozone has been combined with a treatment with a small amount of peracid, which was found to substantially reduce the alkali instability caused by the initial ozone treatment of the pulp. The intention builds on the fact that the combination step can be adapted to the apparatur solution, which was presented for HC ozone steps, see USA 5 181 989. It was shown that the relatively limited peracid treatment, which is a prerequisite of the actual combination step, can be carried out in the normal treatment volume for more diluted pulp, in order to extract soluble lignin at slightly increased pH and, respectively, to treat the pulp with chelating agent in, order to remove disturbing transition metals after the ozone reactor, see patent SE 501 836.

Such combination step involves the difficulty that the ozone treatment must be carried out at low temperature and low pH, preferably 2-3, in order to be selective, while the peracid treatment requlres a relatively high temperature and a higher pH, preferably 4-6. Owing to the fact that the combination step, which is carried out in a HC ozone step with subsequent dilution to a MC system, requires smaller amounts of peracid, because the emphasis is put on the ozone, it has been possible to adapt the conditions to existing HC ozone

step equipment.

Figure 1 describes the system for this combination step. The apparatus equipment is entirely identical with that of a simple HC ozone step, with the exception of the charging equipment for peracid. Figure 1 includes ozone equipment 2, peracid charging equipment 3, a first press 1 and a second press 4.

Figures 2 and 3 illustrate the liquid and temperature balance according to the conditions used according to the invention.

Figures 4 and 5 show the effect of the kappa numbers (which illustrate the lignin content in the pulp) and, respectively, the effect on the pulp viscosity, both directly on the pulp and after a boron hydride reduction of the pulp.

The ozone treatment takes place at a pulp concentration of > 35% and a temperature somewhere between 20 and 60°C. This is a compromise between selectivity requirements, which are furthered by a very low temperature, and to cool the hot white water, without seriously deteriorating the washing efficiency etc. The ozone reaction is extremely rapid and, therefore, the dwell time in the ozone reactor is only one or a few minutes. The pulp is diluted with hot water of a higher pH to a pulp concentration of about 12%, and peracid is added. After a dwell time in a vessel of between 10 and 30 minutes, the pulp is washed. Charged peracid is consumed at a pH between 4 and 6 and a temperature of 60-80°C. Figure 4 shows the effect on the kappa number as a function of the consumption of ozone and, respectively, peracetic acid, both expressed as OXE (1 OXE = the substance amount, which takes up one mole of electrons at the reduction of the substance, 1 kg peracetic acid = 26.3 OXE, 1 kg ozone = 125 OXE). The peracetic acid yields a smaller, but more selective delignification contribution and substantially decreased alkali sensitivity, which at normal viscosity analysis, see Figure 5, yields an increased pulp visco-

sity, especially when the pulp is not boron hydride reduced before the analysis.

CLAIMS

1. A method of bleaching pulp in a combination step with ozone and peracid or salts thereof, such as peracetic acid, **characterized** in that the pulp is ozone treated in a HC step, the pulp is diluted with water or white water, and peracid or salts thereof, such as peracetic acid, are added, whereafter the pulp is treated in a MC bleaching tower.

2. A method according to claim 1, **characterized** in that the pulp is a sulphate pulp with kappa number from 3 to 15, preferably from 5 to 10.

3. A method according to claim 1 or 2, **characterized** in that the amount of ozone added in the HC step is between 0.5 and 10 kg ptp, preferably between 1.5 and 5 kg ptp.

4. A method according to any of claims 1-3, **characterized** in that the amount of added peracetic acid is between 1 and 10 kg ptp, preferably between 2 and 6 kg ptp.

5. A method according to any of claims 1-4, **characterized** in that the pulp being treated has a kappa number in the range of 6.5-8, the ozone amount is in the range of 2-4 kg ptp, and the peracetic acid amount is in the range of 2.5-5 kg ptp.

6. A method according to any of claims 1-5, **characterized** in that the temperature in the ozone step is between 20 and 60°C, preferably between 40 and 50°C.

7. A method according to any of claims 1-6, **characterized** in that the temperature in the peracetic acid step is above or equal to 60°C, preferably 80°C.

8. A method according to any of claims 1-7, **characterized** in that the dwell time in the peracetic step is at least 10 minutes, 15-30 minutes.

AMENDED CLAIMS

[received by the International Bureau on 3 December 1996 (03.12.96); original claims 1, 3 and 4 amended; remaining claims unchanged (2 pages)]

1. A method of bleaching pulp in a combination step with ozone and peracid or salts thereof, such as peracetic acid, **characterized** in that the pulp is ozone treated in a High Consistency step, the pulp is diluted with water or white water, and peracid or salts thereof, such as peracetic acid, are added in an amount between 0.5 and 10 kg ptp, whereafter the pulp is treated in a Medium Consistency bleaching tower.

2. A method according to claim 1, **characterized** in that the pulp is a sulphate pulp with kappa number from 3 to 15, preferably from 5 to 10.

3. A method according to claim 1 or 2, **characterized** in that the amount of ozone added in the High Consistency step is between 0.5 and 10 kg ptp, preferably between 1.5 and 5 kg ptp.

4. A method according to any of claims 1-3, **characterized** in that the amount of added peracetic acid is between 2 and 6 kg ptp.

5. A method according to any of claims 1-4, **characterized** in that the pulp being treated has a kappa number in the range of 6.5-8, the ozone amount is in the range of 2-4 kg ptp, and the peracetic acid amount is in the range of 2.5-5 kg ptp.

6. A method according to any of claims 1-5, **characterized** in that the temperature in the ozone step is between 20 and 60°C, preferably between 40 and 50°C.

7. A method according to any of claims 1-6, **characterized** in that the temperature in the peracetic acid step is above or equal to 60°C, preferably 80°C.

8. A method according to any of claims 1-7, **characterized** in that the dwell time in the peracetic step is at least 10 minutes, 15-30 minutes.

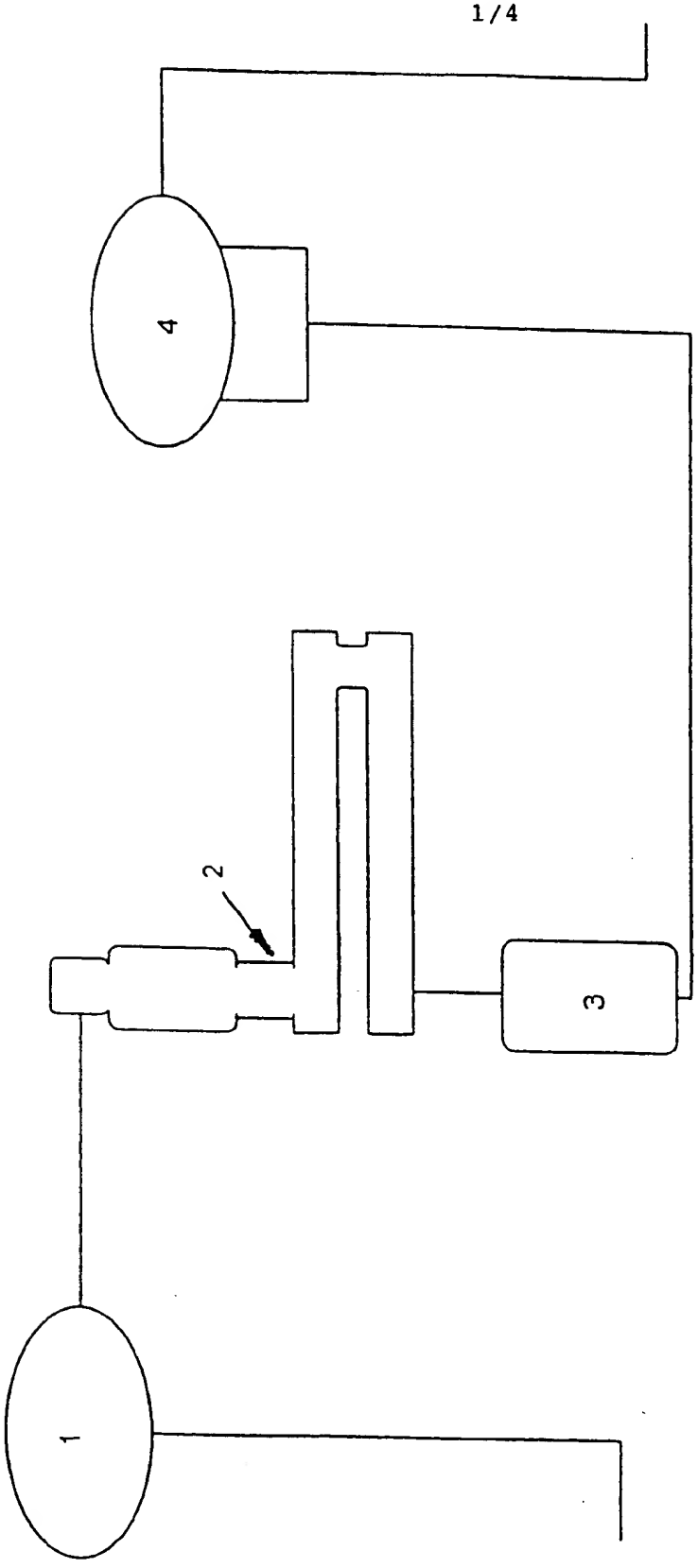
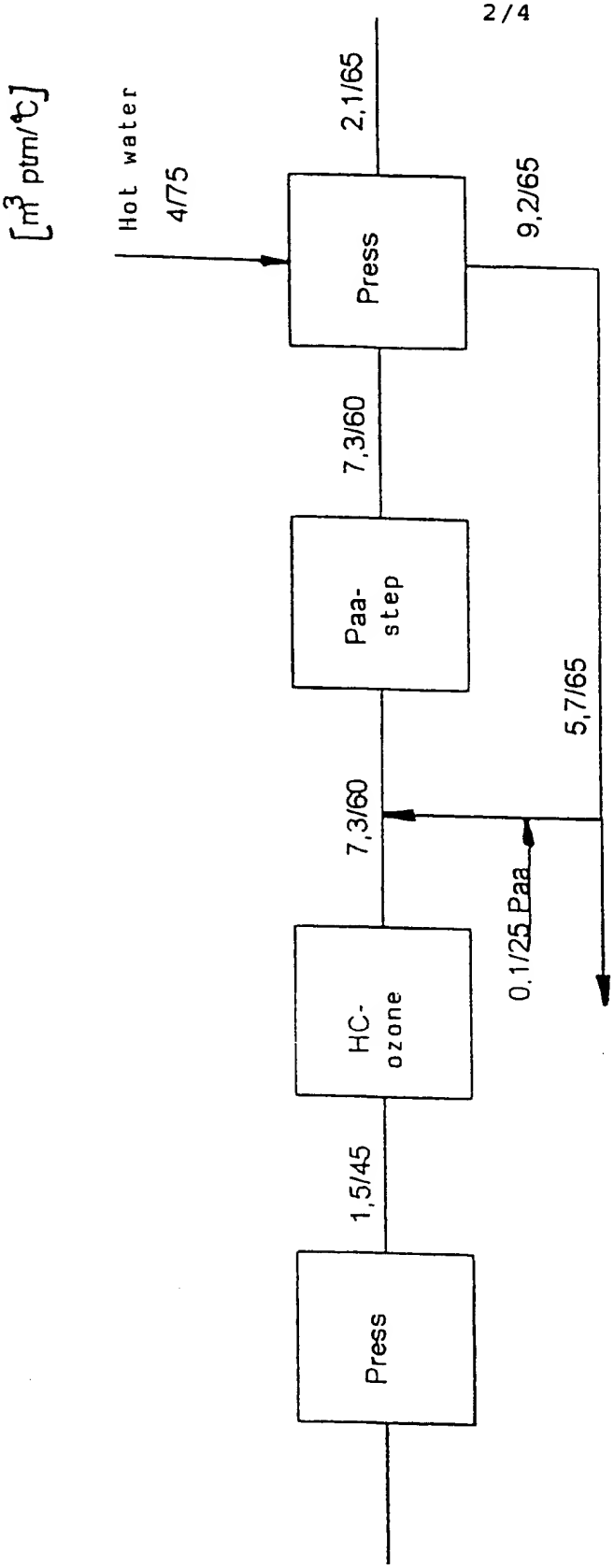


Fig 1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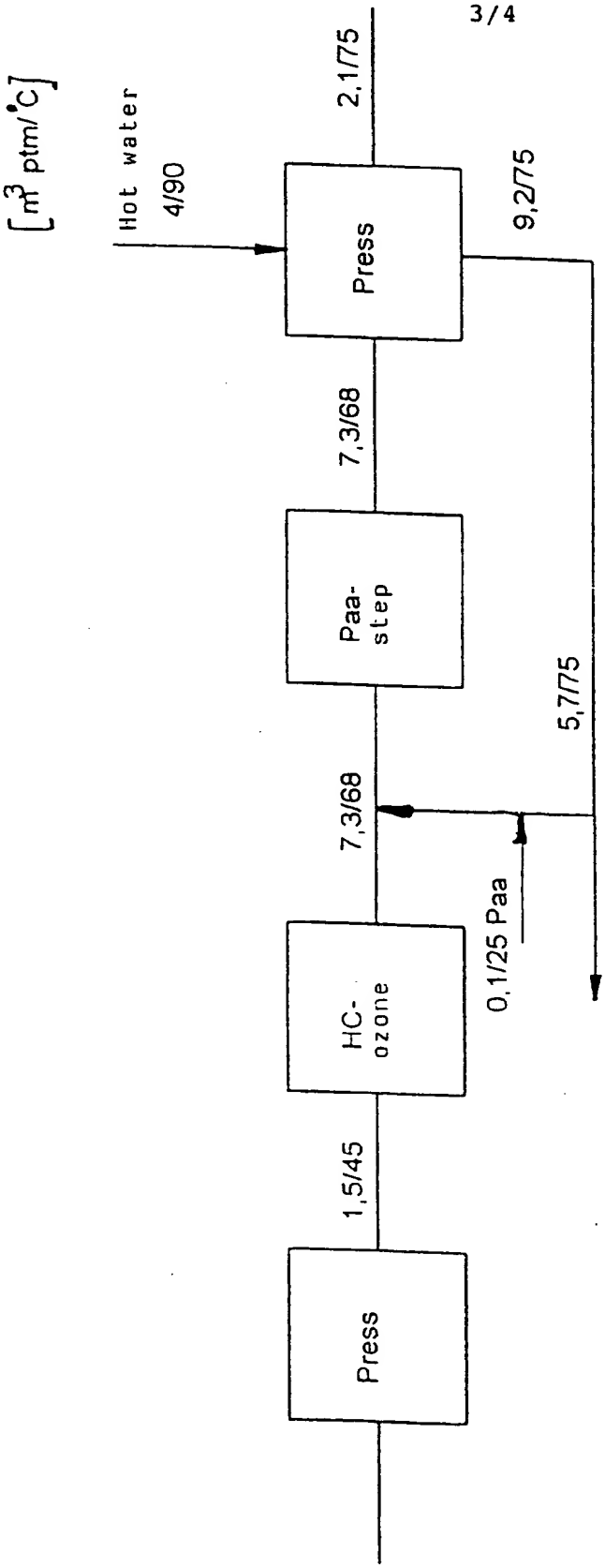
4/75
2,1/65
Press
9,2/65
7,3/60
Paa-step
5,7/65
7,3/60
0,1/25 Paa
HC-ozone
1,5/45
Press

Fig 2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4/90
2,1/75
Press
9,2/75
7,3/68
Paa-step
5,7/75
7,3/68
0,1/25 Paa
HC-ozone
1,5/45
Press

Fig 3

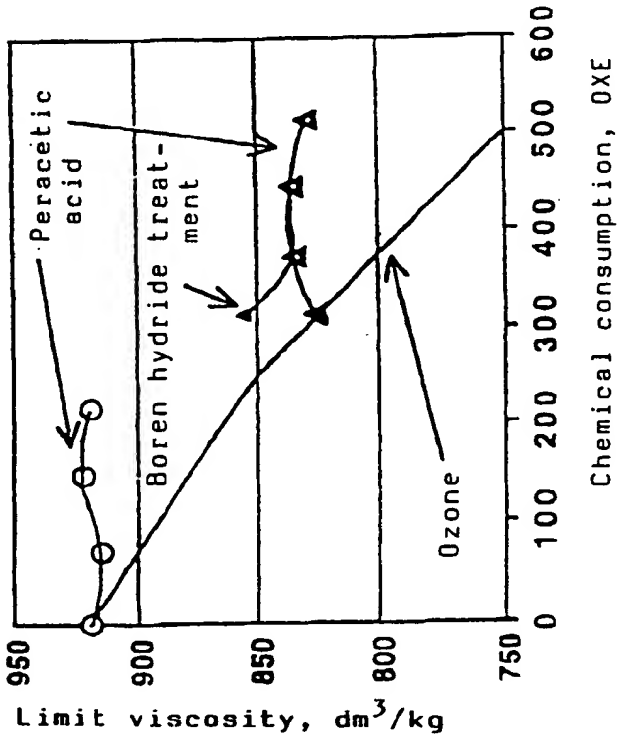
Peracetic acid
Boren hydride treat-ment
Ozone
Chemical consumption, OXE
0
100
200
300
400
500
600
950
900
850
800
750
Limit viscosity, dm3/kg

Fig 5

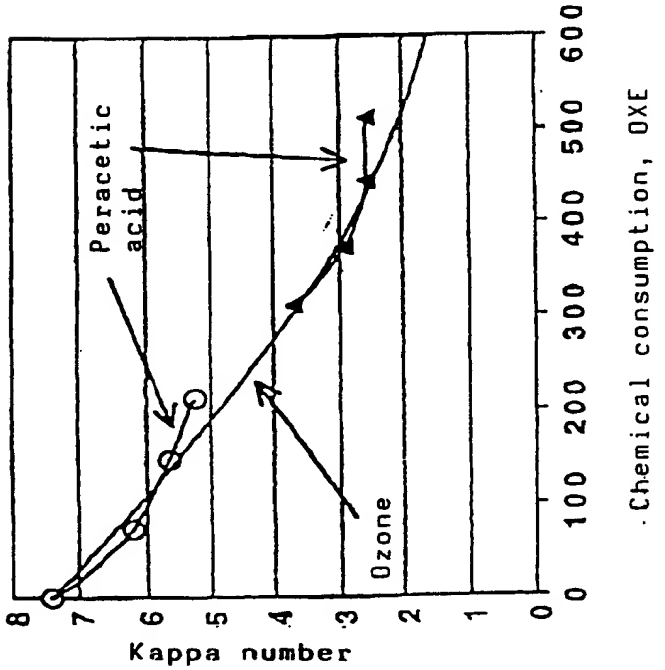
Peracetic acid
Ozone
Chemical consumption, OXE
0
100
200
300
400
500
600
8
7
6
5
4
3
2
1
0
Kappa number

Fig 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 96/00882

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/153, D21C 9/16
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9221814 A1 (INTEROX INTERNATIONAL), 10 December 1992 (10.12.92), page 10, line 12 - page 11, line 11	1-3,6-8
A	FR 2692917 A1 (L'AIR LIQUIDE), 31 December 1993 (31.12.93)	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
1 October 1996	07 -10- 1996
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Marianne Bratsberg Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/09/96

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 9221814	10/12/92	AT-T-	127179	15/09/95
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		FI-D-	935422	00/00/00
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		NO-A-	934406	26/01/94
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FR-A1- 2692917	31/12/93	NONE		